Phosphane Complexes of Alkaline Earth Metals

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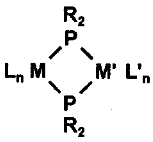
The reaction of lithium[bis(dimethylphosphanyl)(trimethylsilyl)methanide] $Li[(PMe_2)_2C(SiMe_3)]$ with $BeCl_2$ gave the homoleptic compound $Be[(PMe_2)_2C(SiMe_3)]_2$ (**5**) with four beryllium–phosphorus bonds constituting a distorted tetrahedron around the beryllium center. The reaction of $MgCl_2$ with $Li[(PMe_2)_2C(SiMe_3)]$ resulted in the formation of the bis-chelate complex $Mg[(PMe_2)_2C(SiMe_3)]_2 \cdot 2$ THF (**7**), where the distorted *cis*-octahedral magnesium center is additionally coordinated by two THF ligands. In the reaction of **7** with an additional equivalent of $Li[C(PMe_2)_2(SiMe_3)]$, THF is released and the magnesate anion $\{Mg[(PMe_2)_2C(SiMe_3)]_3\}^-$ (**8**) was obtained. This compound is not only the first reported hexacoordinated magnesate, but also the first magnesium compound with six magnesium–phosphorus bonds. With $CaCl_2$ and $Li[C(PMe_2)_2(SiMe_3)]$, a heptacoordinated complex $Ca[(PMe_2)_2C(SiMe_3)]_2 \cdot 3$ THF (**10**) with three coordinating THF ligands was isolated. The complexes were characterized using $^9Be\{^1H\}$-, $^{31}P\{^1H\}$-, ^1H-, $^{13}C\{^1H\}$-NMR spectroscopy, and elemental analysis and by X-ray diffraction. The neutral compounds are highly soluble in nonpolar solvents.

Introduction

The alkaline earth metals are very hard coordination centers. In general, they do not form stable complexes with soft donors such as phosphanes and it seems a challenging task to create stable alkaline earth metal–phosphane donor bonds. Only three complexes of diorganometal centers R_2M with “normal” (i.e. neutral) phosphane ligands R_3P, two examples for beryllium[1] and one for magnesium[2], have been reported in the literature, but none have been well characterized. Phosphane complexes of alkaline earth metals are promising precursors for chemical vapor deposition (CVD) processes and possible candidates for metal-mediated organic synthesis. Moreover, with phosphane donor ligands it might be possible to stabilize low-valency alkaline earth metal compounds and mixed alkaline earth/transition-metal bi- or multinuclear complexes. A promising strategy for creating alkaline earth metal to phosphorus bonds makes use of *anionic* phosphanide ligands containing phosphorus of formal valency number two, and in fact several alkaline earth metal compounds with phosphanide ligands **1** have been described[3]. Bridged heterobimetallic phosphanides **2** may also be formed in this way[4].

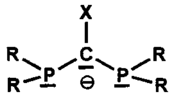
$M[(PR_2)_2]\cdot L_n$

1



2

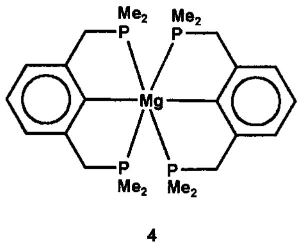
An alternative class of anionic phosphane donor ligands is established by diphosphanomethanides **3**[5].



3

In this class of ligands, in contrast to phosphanides, the negative charge is not localized at the phosphorus atom and the phosphorus valency number is three, as is typical for phosphanes. Anionic diphosphanomethanides have been ligated to hard metal centers (e.g. aluminium[6] and rare earth metals[7]) and they often enable high phosphane coordination numbers even at these metal centers.

Thus, it emerged that phosphane coordination to alkaline earth metals might be achieved by using anionic diphosphanomethanide ligands. Meanwhile, using a related strategy, a hexacoordinated magnesium compound **4** with four magnesium–phosphorus bonds has been successfully synthesized[8].



4

The use of diphosphanomethanides additionally might provide access to homoleptic species exhibiting exclusively metal–phosphorus bonds. Furthermore, the monoanionic nature of these ligands and their tendency to form four-

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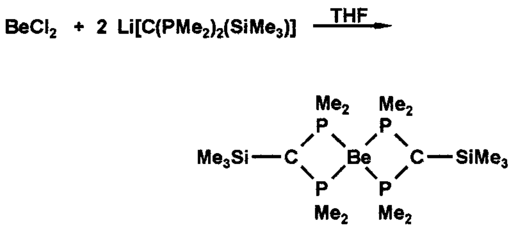
membered chelates allows comparisons to be made with other recently synthesized compounds of alkaline earth metals derived from amidinates and aminoiminophosphoranates[9]. Additionally, for the heavier alkaline earth metals the question of d-orbital participation may be considered.

This paper is concerned with the synthesis and full characterization of phosphane donor adducts to alkaline earth metal centers ranging from beryllium to calcium, including the first homoleptic examples of beryllium and magnesium with exclusive metal−phosphorus bonds.

Results and Discussion

$Be[(PMe_2)_2C(SiMe_3)]_2$ (5)

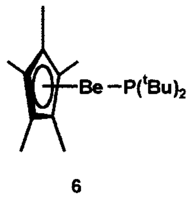
This first molecular compound with beryllium exclusively joined to phosphorus was obtained by treating anhydrous $BeCl_2$ with two equivalents of $Li[(PMe_2)_2C(SiMe_3)]$ according to Eq. (1) and isolated from pentane as colorless crystals **5**. The substance is extremely air and moisture sensitive.



(eq.1)

5

The first $^9Be\{^1H\}$-NMR spectrum of a beryllium−phosphorus compound was obtained from **5** in C_6D_6 at room temperature. It exhibits a quintet at $\delta = 6.4$ with a $^1J_{Be-P}$ coupling constant of 33.5 Hz. The same coupling constant can be extracted from the $^{31}P\{^1H\}$-NMR quartet signal ($\delta = -30.8$). This is an indication of a highly symmetrical structure with four equivalent phosphorus atoms in solution. As expected, the coupling constant is smaller than that observed in the $^{31}P\{^1H\}$-NMR spectrum of the phosphanide compound Cp*BeP(*t*Bu)$_2$ (**6**) ($^1J_{Be\text{-}P} = 50$ Hz), the only other hitherto known, sufficiently characterized molecular beryllium−phosphorus compound[10].



6

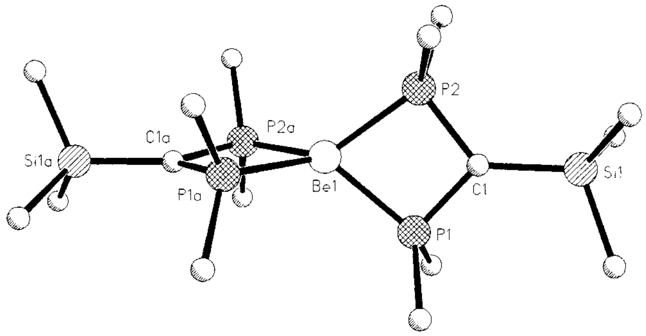
The spectra are essentially temperature independent (−80 to +40°C).

X-ray analysis reveals 1/2 (**A**) and 1/4 (**B**) molecule in the asymmetic unit. The whole molecules can be generated by symmetric transformations (#1: $x + 1 - 1$, $-y + 1/2$, $-z + 3/2$; #2: $-x$, y, $-z + 1/2$; #3: $-x + 1 - 1$, $-y + 1/2$, z; #4: $-x$, y, $-z + 3/2$). The bond lengths and angles are nearly identical for both molecules **A** and **B**, but the $SiMe_3$ group in **B** is disordered and could not be resolved computationally. Therefore, only molecule **A** will be discussed.

In the solid state, compound **5** is a monomer. The central beryllium dication is coordinated by two chelating $[(PMe_2)_2C(SiMe_3)]^-$ monoanions resulting in a distorted tetrahedral BeP_4 arrangement. The normals to the two BeP_2 planes intersect at an angle of 90°. Both BePCP four-membered rings are planar, as is the environment of the endocyclic C atoms C1 and C1a. The Be−P bond lengths are remarkably short; a comparison with the only two structurally characterized beryllium−phosphorus compounds shows that the bond lengths in **5** [2.134(2) and 2.137(3) Å] are just between the respective bond lengths in **6** (2.083 Å)[10] and in the binary solid-state phase Be_3P_2 (2.20 Å)[11], but in both cases anionic phosphanide- and phosphide-type ligating atoms, respectively, are involved.

The endocyclic P−C bond lengths [1.740(4) and 1.744(4) Å] are quite short and of nearly equal length, as is the case in a variety of other diphosphanomethanide complexes[5]. This has been explained in terms of an ylidic bonding model with some charge delocalization within the PCP moiety. The nonbonding P1−P2 distance [2.685(1) Å] is significantly shorter than the van der Waals radii, as is the case with other chelating diphosphanomethanide derivatives and must be regarded as a consequence of the geometric restraints[12].

Figure 1. Crystal structure of **5** (only molecule A is shown)

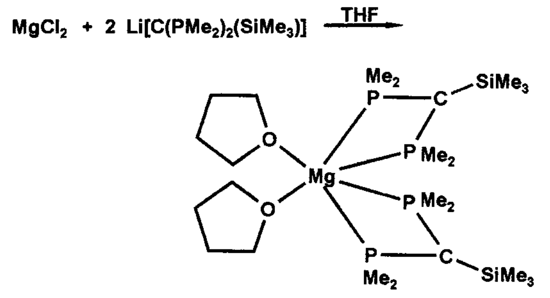


$Mg[(PMe_2)_2C(SiMe_3)]_2 \cdot 2$ THF (7)

Diphosphanomethanides can span tetrahedral coordination sites only with centers from the second period (lithium[13], beryllium: this paper, boron[14]). With increasing atomic radii, i.e. with the heavier elements, either higher coordination numbers at the coordination center M (which decreases the P−M−P angle; Si[15], P[12]) or a monodentate ligating mode is observed (Si[15], P[16]). Consequently, in the analogous reaction of anhydrous $MgCl_2$ with $Li[(PMe_2)_2C(SiMe_3)]$, the formation of the bis-chelate complex **7** is observed.

In contrast to the beryllium compound, where the central atom is tetrahedrally coordinated by four phosphorus atoms, the magnesium center in **7** is additionally coordinated by two THF molecules, completing a distorted octahedral environment at the metal center.

$^{31}P\{^1H\}$-NMR variable-temperature experiments at −80°C show a multi-line, symmetric pattern, tentatively assigned to a not completely resolved AA′BB′ spin system

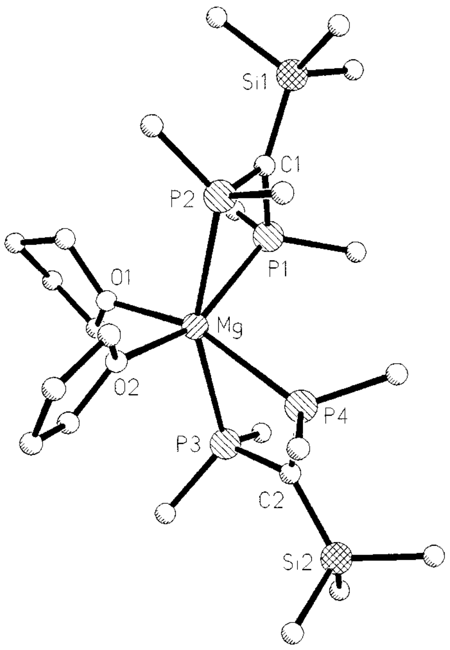


(eq.2)

7

(centered at δ = −16.7). At room temperature only one singlet (δ = −16.2) was detected, due to a fast exchange of axial and equatorial sites. These experiments indicate a *cis*-octahedral coordination, in contrast to the only hitherto known magnesium−phosphorus compound **4** with four Mg−P bonds[8]. The *cis*-octahedral coordination was confirmed by X-ray analysis.

Figure 2. Crystal structure of 7



The Mg−P bond lengths [2.654(1)−2.684(1) Å] are equal within one standard deviation and are significantly shorter than in **4** [2.761(1) and 2.770(1)[8]], but more comparable with those in tetracoordinated magnesium−phosphanide compounds, e.g. in [Mg(PHPh)$_2$(TMEDA)] [2.592(5) and 2.587(5) Å][17].

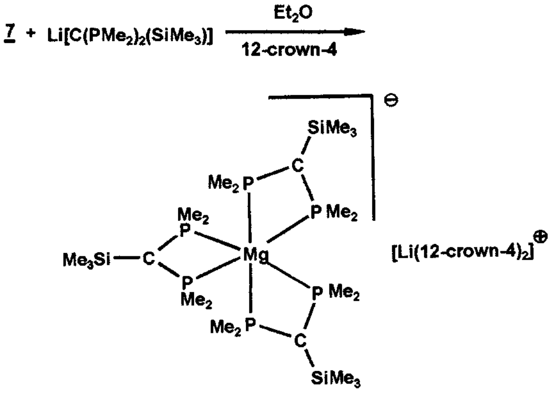
In contrast, the Mg−O bond lengths [2.137(2) and (2.122(2) Å] are significantly longer than in tetrahedral reference compounds [e.g. Ph$_2$Mg(THF)$_2$: 2.03 Å][18], and therefore it seems possible to remove the THF ligands. In fact, a substitution of the THF ligands by a third diphosphanomethanide ligand is possible (see below).

The average bond lengths of P1/2−C1 and P3/4−C2 (1.75 Å) range between the bond lengths of an ylidic P−C bond (typically around 1.68 Å) and a single P−C bond (ca. 1.83 Å), consistent with the carbanionic character of C1 and C2. The mean lengths of P−C$_{methyl}$ bonds (1.85 Å) are roughly within this latter range.

The sums of the angles in the four-membered rings MgPCP are 359.8° and 359.9° respectively, which indicates the planarity of chelate rings. The environment of the carbanionic carbon atoms is also planar, the silicon atom of the SiMe$_3$ groups adopting a position in the same plane as the four-membered chelate rings.

$[Li(12\text{-}crown\text{-}4)_2]^+\{Mg[(PMe_2)_2C(SiMe_3)]_3\}^-$ (8)

The homoleptic "magnesate" anion **8** is obtained as described in Eq. 3. Hitherto known "magnesate" anions exhibit coordination numbers of four[19] or five[20]. It is also the first molecular magnesium compound with six magnesium−phosphorus bonds.



(eq.3)

8

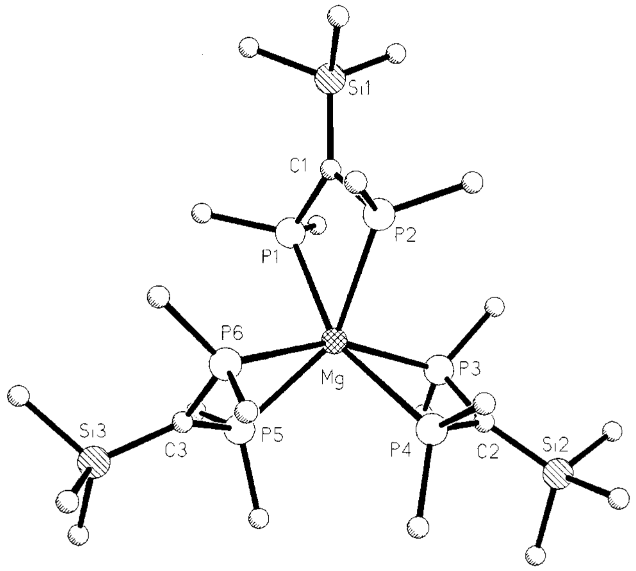
The $^{31}P\{^1H\}$-NMR spectrum (C_6D_6) shows a singlet (δ = −15.8), which does not vary with temperature and thus indicates the equivalence of all six phosphorus atoms.

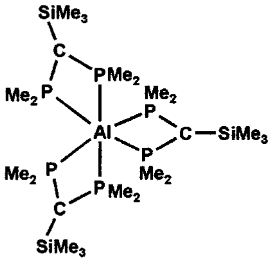
The ^1H-NMR spectrum (C_6D_6) reveals, besides the signals of the phosphanomethanide ligand, the presence of two 12-crown-4 molecules (δ = 2.9) per anion. Colorless crystals of **8** have been grown from diethyl ether solution. The X-ray analysis shows the structure containing a Li[12-crown-4]$_2^+$ cation[21], two molecules of C_6H_6 and a hexacoordinated "magnesate" anion, which is isoelectronic with the neutral aluminium complex **9**[6]. The cation and anion units are well separated without any noticeable interionic contacts.

The Li[12-crown-4]$_2^+$ cation shows considerable disorder, which influences the *R* values, but has no influence on the structural findings concerning the anion. Again, as in **5** and **7**, the three four-membered chelate rings in **8** are planar, as are the environments of the carbanionic carbon atoms. The deviation from the ideal octahedral geometry at magnesium can be described by the torsion angle ϕ of the trigonal P$_3$ planes P1, P3, P5 and P2, P4, P6 (ϕ = 32.2°). This angle indicates a slightly enhanced torsion towards a trigonal-prismatic coordination compared to **9** (ϕ = 35.9°)[6].

A magnesium ion of coordination number six can also be assigned in the polymeric solid-state phase of MgP$_4$[22],

Figure 3. Crystal structure of **8** (only the anion is shown)





9

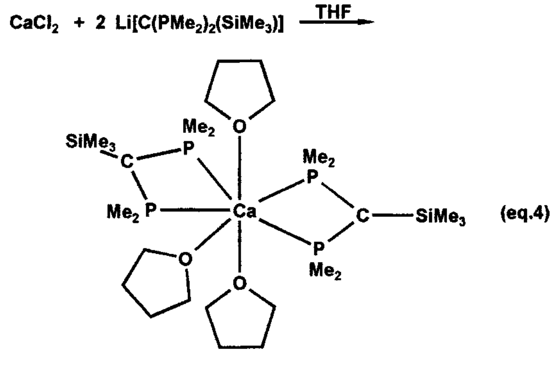
although a description in terms of 4 + 2 coordination may be more appropriate. There are two quite different Mg−P distances in MgP_4 (four short contacts: 2.608 A and two long contacts: 2.862 A), in marked contrast to the case of **8**. In **8**, the Mg−P bond lengths are more similar, ranging from 2.635(3) to 2.698(3) A, with a mean Mg−P bond length of 2.66 A. In **9**, the Al−P distance amounts to 2.490 A[6]. Altogether, as expected, a high ionic contribution to the metal to ligand bonding in both **8** and **9** may be extracted from these data.

$Ca[(PMe_2)_2C(SiMe_3)]_2 \cdot 3$ THF

The diphosphanomethanides are also suitable phosphane donor ligands for the heavier alkaline earth metals. An example is given by Eq. 4. Colorless crystals of **10** are obtained from the pentane extraction of the reaction mixture.

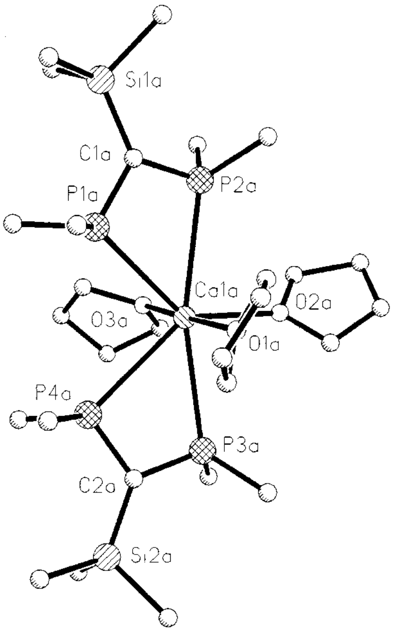
The $^{31}P\{^1H\}$-NMR spectrum displays a singlet ($\delta = -28.6$) which essentially remains unchanged on cooling (−80 °C).

The X-ray analysis of the colorless crystals of **10** shows two identical molecules in the asymmetric unit and reveals phosphane coordination to a calcium atom for the first time. Three THF molecules and two chelating diphosphanomethanide ligands generate a distorted pentagonal-bipyramidal coordination polyhedron. Two of the THF ligands are in a *trans*-axial position with a bond angle O1−Ca1−O3 of 177.0(1)°; the third THF ligand and the two planar four-membered chelate rings of the diphosphanomethanides complete the pentagon. The sum of internal angles is 361.3° indicating the near planarity of the pentagon. The higher coordination number of Ca^{2+} can easily be understood in terms of the increasing ion radius in going from Mg^{2+} to Ca^{2+}.



10

Figure 4. Crystal structure of **10** (only molecule A is shown)



The angles P2−Ca1−O2 and P3−Ca1−O2 are close to rectangular (81.96° and 81.95°, respectively) indicating that the two chelating diphosphanomethanide ligands are located essentially in one hemisphere of the central atom, as is the case in the magnesium compound **7** (which in the case of **10** is more or less trivial, however). The partial ylidic character of the $P-C_{carbanion}$ bond again is evident from the average bond lengths of 1.75 A (see above). The mean Ca−P (3.043 A) and Ca−O bond lengths (2.391 A) are within the range found in known phosphanide and THF complexes of calcium[3][23]. An indication of d-orbital participation is not obvious, at least as extracted from the planarity of the chelate rings and of the endocyclic C atoms, as it also was found in most other diphosphanomethanide complexes, including **5**, **7**, **8**, and **9**. In marked contrast to **10**, the chelate rings in the scandium complex $Sc[(PMe_2)_2C(SiMe_3)]_3$[7] show a considerable deviation from planarity.

Comparison of 5, 7, and 10

All three compounds are monomeric and contain chelating diphosphanomethanides. As a consequence of the monomeric nature, these alkaline earth metal−phosphane complexes are soluble in nonpolar organic solvents such as pentane. With increasing metal radii, the coordination number increases from 4 (beryllium) to 6 (magnesium) to 7 (calcium), resulting in more or less distorted tetrahedral, octahedral, and pentagonal-bipyramidal coordination geometry, respectively. The additional coordination sites are occupied by two (magnesium) or three (calcium) THF donor molecules. In all cases the four-membered chelate rings including the metal atom are planar. For the magnesium and the calcium compounds a cisoid coordination of the diphosphanomethanide ligands is observed. The P−C bond lengths within the four-membered rings in all cases are close to 1.75 A which is well between the bond lengths of a single and an ylidic P−C double bond. This is in accordance with other diphosphanomethanide chelate rings and reflects the partial ylidic character of this bond. Since all P−C and M−P endocyclic bond lengths within a given compound are almost identical, an "unisobidentate" coordination mode, as present in some diphosphanomethanide[14] and related complexes with potentially bidenate ligands[24], is not observed. One may speculate whether the restriction of the diphosphanomethanide coordination to one hemisphere of the metal (magnesium, calcium) may be attributed to effects which are also responsible for the bending in simple MX_2 molecules[25]. It is interesting to note that similar behavior has been observed in amidinate and aminoiminophosphoranate complexes of the heavier alkaline earth metals[9]. This observation can now be extended: it is no longer restricted to N-donor-type ligands, but includes also P-donor-type ligands and is probably a quite general phenomenon. Moreover, magnesium coordination centers can also be added to the series, which is particularly noteworthy since d orbitals are not available for this element.

The proposed generality of this observation is augmented by the fact that the chelate rings in **5**, **7**, and **10** not only span quite different coordination polyhedra but also vary considerably in the M−P bond lengths in going from beryllium to magnesium to calcium. Likewise, as a consequence of this bond lengthening, the endocyclic angles at phosphorus increase and at the metal decrease (see Table 1). Hence, although the geometric constraints are quite different, the cisoid arrangement of the anionic ligands is retained.

Comparison of 7 and 8

The replacement of the two THF ligands in **7** by a third diphosphanomethanide ligand leads to the first reported hexacoordinated "magnesate" anion **8** with six magnesium−phosphorus bonds.

The Mg−P bond lengths in both compounds are nearly equal, as are the bond lengths and angles in all four-membered chelate rings. This shows that the anionic nature of **8** has no influence on the radius of the Mg^{2+} dication; the bonding thus seems to be mainly ionic.

In accord with the long Mg−O bonds in **7**, the THF ligands can be removed thermally by heating **7** in vacuo. However, a simple THF-free derivative of **7** was not ob-

Table 1. Comparison of structural features of **5**, **7**, **8**, and **10**

$Be[(PMe_2)_2C(SiMe_3)]_2$, **5** (molec. A)	$Mg[(PMe_2)_2C(SiMe_3]_2 \cdot 2$ THF, **7**	$\{Mg[(PMe_2)_2C(SiMe_3]_3\}^-$, **8**	$Ca[(PMe_2)_2C(SiMe_3]_2 \cdot 3$ THF, **10** (molec. A)
Be−P1: 2.137(3)	Mg−P1: 2.667(1)	Mg−P1: 2.635(3)	Ca−P1: 3.041(1)
Be−P2: 2.134(3)	Mg−P2: 2.678(1)	Mg−P2: 2.689(3)	Ca−P2: 3.049(1)
	Mg−P3: 2.654(1)	Mg−P3: 2.674(3)	Ca−P3: 3.045(1)
	Mg−P4: 2.684(1)	Mg−P4: 2.668(3)	Ca−P4: 3.038(1)
	Mg−O1: 2.137(2)	Mg−P5: 2.644(3)	Ca−O1: 2.393(3)
	Mg−O2: 2.122(2)	Mg−P6: 2.682(3)	Ca−O2: 2.410(3)
			Ca−O3: 2.370(3)
P1−C1: 1.740(4)	P1−C1: 1.752(2)	P1−C1: 1.753(9)	P1−C1: 1.758(4)
P2−C1: 1.744(4)	P2−C1: 1.750(2)	P2−C1: 1.766(8)	P2−C1: 1.758(4)
	P3−C2: 1.753(2)	P3−C2: 1.754(7)	P3−C2: 1.765(4)
	P4−C2: 1.753(2)	P4−C2: 1.753(7)	P4−C2: 1.751(4)
		P5−C3: 1.761(7)	
		P6−C3: 1.745(8)	
P1−Be−P2: 77.92(4)	P1−Mg−P2: 63.48(2)	P1−Mg−P2: 63.55(8)	P1−Ca−P2: 55.62(3)
Be−P1−C1: 90.6(2)	Mg−P1−C1: 94.93(7)	Mg−P1−C1: 96.5(3)	Ca−P1−C1: 98.4(1)
Be−P2−C1: 90.5(2)	Mg−P2−C1: 94.61(7)	Mg−P2−C1: 94.3(3)	Ca−P2−C1: 98.1(1)
P1−C1−P2: 100.9(2)	P1−C1−P2: 106.8(1)	P1−C1−P2: 105.7(4)	P1−C1−P2: 107.8(2)
	P3−Mg−P4: 63.69(2)	P3−Mg−P4: 63.36(7)	P3−Ca−P4: 55.20(3)
	Mg−P3−C2: 95.16(8)	Mg−P3−C2: 95.0(2)	Ca−P3−C2: 98.2(1)
	Mg−P4−C2: 94.12(7)	Mg−P4−C2: 95.2(2)	Ca−P4−C2: 98.8(1)
	P3−C2−P4: 106.9(1)	P3−C2−P4: 106.3(3)	P3−C2−P4: 106.5(2)
P1−Be−P1$^{\#}$: 124.8(3)	P3−Mg−P2: 157.04(3)	P5−Mg−P6: 63.47(8)	P3−Ca−P2: 163.89(4)
P1−Be−P2$^{\#}$: 126.61(5)	P3−Mg−P1: 102.18(3)	Mg−P5−C3: 95.6(3)	P3−Ca−P1: 140.46(4)
P2−Be−P1$^{\#}$: 126.61(5)	P4−Mg−P2: 100.03(3)	Mg−P6−C3: 94.7(3)	P4−Ca−P2: 140.61(4)
P2−Be−P2$^{\#}$: 130.6(3)	P4−Mg−P1: 101.18(3)	P5−C3−P6: 106.1(4)	P4−Ca−P1: 86.12(4)

Table 2. Crystal data of **5**, **7**, **8,** and **10**

	5	**7**	**8**	**10**
formula	$C_{16}H_{42}BeP_4Si_2$	$C_{24}H_{48}MgO_2P_4Si_2$	$C_{40}H_{95}MgLiO_8P_6Si_3\cdot 2\ C_6H_6$	$C_{28}H_{66}CaO_3P_4Si_2$
formula weight	423.571	583.071	1161.721	670.951
space group	*Ccca*	$P2_1/c$	$P2_1/c$	$P2_12_12_1$
crystal system	orthorhombic	monoclinic	monoclinic	orthorhombic
a [Å]	18.230(1)	16.934(1)	12.567(1)	17.309(2)
b [Å]	28.256(2)	12.556(1)	24.569(2)	20.907(2)
c [Å]	15.963(1)	18.591(2)	24.987(2)	22.583(2)
α [°]	90	90	90	90
β [°]	90	116.0(1)	101.1(1)	90
γ [°]	90	90	90	90
Z	12	4	4	8
ρ ($mg\cdot m^{-3}$)	1.026	1.090	1.019	1.091
μ (mm^{-1})	0.361	0.315	0.237	0.393
F(000)	2760	1272	2520	2928
2θ range (deg)	6−50	6−50	6−48	6−50
reflections collected	7746	6920	12118	15054
reflections unique	4018	6198	11830	14266
refined params	163	312	661	713
GooF[a] s on F^2	1.034	1.026	1.056	1.020
$R1[F_0>4\sigma(F_0)]$[b]	0.056	0.036	0.095	0.046
$wR2[F_0>4\sigma(F_0)]$[b]	0.149	0.092	0.286	0.095
Largest diff. peak and hole [$e\cdot Å^{-3}$]	0.576, −0.485	0.614, −0.274	1.563, −0.389	0.400, −0.204

[a] Definition of the *R* values: $R1 = (\Sigma\|F_o| - |Fc\|)/\Sigma|F_o|$, $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2$ – [b] Definition of goodness-of-fit, *s*: $s = \{\Sigma[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

tained, the nature of the resulting compound being currently under investigation.

Conclusion

For the first time it has been demonstrated that not only phosphanide donors (with two-coordinated phosphorus), but also "normal" phosphane donors (with three-coordinated phosphorus) are able to coordinate to alkaline earth metal centers. Even "classic" ligands for alkaline earth metals, such as halides, diethylether, or THF can be replaced successfully by diphosphanomethanides. These results emphasize the exceptional role of diphosphanomethanides in phosphane coordination chemistry. The preference for a cisoid arrangement of anionic ligands in alkaline earth metal compounds can be emphasized and further extended. This seems to be a quite general phenomenon that is not restricted to the heavier metal centers but has now also been established for magnesium compounds.

The neutral compounds described are soluble in nonpolar solvents and represent promising precursors for chemical vapor deposition (CVD) processes. In addition they are possible candidates for metal-mediated organic synthesis and for a wide range of reactions in nonpolar solvents.

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Experimental Section

General: All reactions were performed in a two-armed glass vessel as described elsewhere[26]. Exclusion of air and moisture was essential and glassware was treated accordingly. All solvents were dried over Na/K alloy and distilled prior to use. – For ^1H- and $^{13}C\{^1H\}$-NMR spectra TMS (δ = 0) was used as an internal standard. The $^{31}P\{^1H\}$-NMR spectra were obtained in C_6D_6 ([D_8]toluene for low temperature experiments) with H_3PO_4 (85%) as the external reference on a JEOL GX 270 spectrometer. The ^9Be-NMR spectrum was obtained in C_6D_6 with $BeSO_4\cdot 7\ H_2O$ as the external standard on a JEOL Lambda 400 spectrometer.

The alkaline earth metal chlorides were used in the anhydrous form and prepared as described[27]. 12-crown-4 was purchased from commercial sources and dried over molecular sieve (4 A). $Li[(PMe_2)_2C(SiMe_3)]$ was prepared as described previously[28].

Elemental analyses were performed by the Mikroanalytisches Labor des Anorganisch-chemischen Instituts der Technischen Universität München.

Hazard: Beryllium compounds are extremely toxic and may cause cancer[29]. Handle with care! Avoid inhalation and any skin contact!

Preparation of the Diphosphanomethanide Complexes with Be, Mg, and Ca: 7.0 mmol of $Li[(PMe_2)_2C(SiMe_3)]$[28] and 3.5 mmol of MCl_2 (M = Be, Mg, Ca) were dissolved in 40 ml of THF at −78 °C. After being stirred overnight at room temperature, the solvent was removed and replaced by pentane. After filtration, colorless crystals were isolated from pentane in all cases by slowly cooling the solutions.

Preparation of $[Li(12\text{-}crown\text{-}4)_2]^+\{Mg[(PMe_2)_2C(SiMe_3)]_3\}^-$: 2.20 mmol of $Li[(PMe_2)_2C(SiMe_3)]$[28] were dissolved in ether (40 ml) at −78 °C. After adding 2.20 mmol of 12-crown-4 and 2.06 mmol of $Mg[(PMe_2)_2C(SiMe_3)]_2\cdot 2$ THF (**7**), the mixture was warmed up to room temperature and stirred overnight. The ether was removed and the remaining solid was washed with 30 ml of pentane. After replacing pentane by ether, colorless crystals were grown from the solution by cooling.

All compounds were extremely air and moisture sensitive. Therefore, elemental analysis were not completely satisfactory in all cases.

$Be[(PMe_2)_2C(SiMe_3)]_2$ (**5**): M = 423.571 g/mol, yield: 87.2%. − ^{1}H (C_6D_6): δ = 0.20 (s, 18 H), 1.21 (s, 24 H). − $^{31}P\{^1H\}$ (C_6D_6): δ = −30.8 (1:1:1:1 quart., $^1J_{Be-P}$ = 33.5 Hz). − $^{13}C\{^1H\}$ (C_6D_6): δ = 4.70 [s, $Si(CH_3)_3$] 20.17 ["quint.", $P(CH_3)_2$], 22.31 (s, $P_2\mathit{C}Si$). − ^{9}Be (C_6D_6): δ = 6.4 (quint., $^1J_{Be-P}$ = 33.5 Hz). − $C_{16}H_{21}BeP_4Si_2$: calcd. (found): C, 45.40 (43.74); H, 10.01 (9.64).

$Mg[(PMe_2)_2C(SiMe_3)]_2 \cdot 2$ THF (**7**): M = 583.071 g/mol, yield: 91.0%. − ^{1}H (C_6D_6): δ = 0.53 (s, 18 H), 1.28 (m, THF, 8 H), 1.36 (s, 24 H), 3.47 (m, THF, 8 H). − $^{31}P\{^1H\}$ (C_6D_6): δ = −16.2 (s); $^{31}P\{^1H\}$ ([D$_8$]toluene, −100°C): δ = −16.7 (AA′BB′ spin system, N = 34.2 Hz). − $^{13}C\{^1H\}$ (C_6D_6): δ = 6.37 [s, $Si(\mathit{C}H_3)_3$], 21.63 ["quint.", $P(\mathit{C}H_3)_2$], 22.67 (s, $P_2\mathit{C}Si$), 25.46 (s, THF), 68.57 (s, THF). − $C_{16}H_{21}MgP_4Si_2$: calcd. (found): C, 49.26 (49.11); H, 10.33 (10.07).

$\{Mg[(PMe_2)_2C(SiMe_3)]_3\}^- Li(12\text{-}crown\text{-}4)_2^+$ (**8**): M = 1005.494 g/mol, yield: 55.0%. − ^{1}H (C_6D_6): δ = 0.40 (s, 27 H), 1.49 (s, 36 H), 2.90 (s, 32 H). − $^{31}P\{^1H\}$ (C_6D_6): δ = −15.5 (s); $^{31}P\{^1H\}$ ([D$_8$]toluene, −80°C): δ = −14.8 (s, br). − $^{13}C\{^1H\}$ (C_6D_6): δ = 6.94 [s, $Si(\mathit{C}H_3)_3$], 22.05 ["quint.", $P(\mathit{C}H_3)_2$], 22.63 (s, $P_2\mathit{C}Si$), 65.46 (s, 12-crown-4).

$Ca[(PMe_2)_2C(SiMe_3)]_2 \cdot 3$ THF (**10**): M = 670.951 g/mol, yield: 85.7%. − ^{1}H (C_6D_6): δ = 0.46 (s, 18 H), 1.27 (m, THF, 12 H), 1.31 (s, 24 H), 3.50 (m, THF, 12 H). − $^{31}P\{^1H\}$ (C_6D_6): δ = −28.6 (s). − $^{13}C\{^1H\}$ (C_6D_6): δ = 7.75 [s, $Si(\mathit{C}H_3)_3$], 21.89 ["quint.", $P(\mathit{C}H_3)_2$], 22.70 (s, $P_2\mathit{C}Si$), 25.58 (s, THF), 68.71 (s, THF). − $C_{28}H_{45}CaO_3P_4Si_2$: calc, (found): C, 50.12 (48.57); H, 9.91 (9.79).

X-ray Measurements: The single crystals were sealed in thin-walled capillaries and mounted on a four-circle diffractometer CAD4 (Fa. ENRAF-NONIUS) with graphite-monochromated Mo-Kα radiation (λ = 0.71073 A). All data were collected at low temperatures (−74°C). The structures were solved by direct methods with the software package SHELXTL PC[30] and refined with the program SHELXL-93[31]. All non-hydrogen atoms were refined anisotropically, and a riding model was employed in the refinement of the hydrogen atom positions. Further details can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen under following CSD-numbers: Be-$[(PMe_2)_2C(SiMe_3)]$ 407270, $Mg[(PMe_2)_2C(SiMe_3)]_2 \cdot 2$ THF 407238, $\{Mg[(PMe_2)_2C(SiMe_3)]_3\}^-\{Li(12\text{-}crown\text{-}4)_2\}^+$ 407252, $Ca[(PMe_2)_2$-$C(SiMe_3)]_2 \cdot 3$ THF 407239.

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